THE COLLOIDAL BEHAVIOUR OF SERICIN. I.

By Hideo KANEKO.

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Introduction.

The crude silk fiber spun by the silk-worm, consists of a filament of fibroin surrounded by a glue-like coating known as sericin. Sericin, also called silk-glue, is one of the proteins secreted from the silkgland by the silk-worm. It swells in cold water, and is readily soluble when boiled. The relative proportion of these two components, fibroin and sericin in crude silk differs considerably with different varieties of cocoons, but generally sericin occupies about 25 per cent. of the raw fiber. Mulder gave formula $C_{15}H_{25}N_5O_8$ to sericin, the elementary composition being C: 43, H: 6, N: 16, and O: 35 per cent.

Sericin is commonly accompanied by small amounts of colouring and mineral matters as well as of fatty and waxy substances. The physico-chemical behaviours of sericin have a great influence on the facility in reeling the raw silk from cocoons. For this reason I have studied some colloidal properties of sericin in its various states and varieties.

To the chemical investigation of silk fiber, especially of the amino acids obtained from it, R. Inoue[1] has contributed, and according to his estimation the percentages of the known constituents of silk-glue are as follows:

	Inner layer (per cent.)	Outer layer (per cent.)
Glycocoll	5.77	2.99
Alanine	8.49	9.24
Tyrosine	5.25	2.85
Serine	2.56	6.33
Phenylalanine	2.66	2.60
Leucine	0.73	2.30
Proline	0.35	—
Aspartic acid	6.81	2.74
Glutamic acid	—	0.94

(1) R. Inoue, *Reports Seric. and Silk Ind. Science*, 1929.

E. Hiratsuka[2] studied completely the properties of liquid silk in the silk-worm. We shall understand by "fine structure" the molecular and micellar constitution of the proteins as revealed or indicated by chemical investigations, by X-ray spectroscopy, and by other investigations.

It is confirmed by the chemical investigations of Fischer that the proteins consist of long chain-like molecules of condensed or peptide amino acids. The natural proteins consist of more or less uniformly oriented crystallites of parallel polypeptide-type chains. Brill (1923),[3] Herzog and Jancke (1927)[4] state that, under X-ray investigation, fibroin has a crystalline character and that it is a mixture of at least one crystalline and several amorphous compounds, the nature of the mixture varying with the sources of the silk.

Meyer and Mark (1928)[5] believe that fibroin consists of four principal valence chains of glycyl-alanine, the length of the micellæ being 150 A. U. and corresponding to a polypeptide of at least twenty glycylalanyl groups. But very little work has been conducted to elucidate the chemical constitution of sericin and it is generally believed that it has an amorphous structure. To the study of its chemical composition Abderhalden and his co-workers[6] have made much contribution. Karrer made a fermentative investigation on fibroin and examined the partial decomposition of sericin by the proteolytic enzymes secreted by some bacteria. E. Furuya has been studying along a similar line in our college. I report here a study of some colloidal behaviours of sericin existing on the cocoon layer and separated from it by boiling in water or by precipitation with an electrolyte.

PART I.

Sec. I. The Solubility of Sericin on the Cocoon Layer.

(1) The Solubility of Sericin in Water. Generally, "kaijo" of cocoons is represented by the weight of raw silk reeled per hour under the same condition. The state and colloidal properties of the sericin particles of the cocoon change in a remarkable manner with the external factors during their gelatinization, drying process or their preservation, and the internal

(2) E. Hiratsuka, *Bull. Imperial Seric. Exp. Station, Japan*, Vol. **1** (1918), 203–224.

(3) Brill, "Ein Beitrag zur chem. Konstitution des Seidenfibroins," 1923; *Naturwissenschaften*, **18** (1930), 622.

(4) Herzog and Jancke, *Z. Physik*, **3** (1920), 196; *Helvetica Chim. Acta*, **11** (1928), 529.

(5) Meyer and Mark, *Ber.*, **61** (1928), 1982; *Z. physik. Chem.*, **2** (1929), 115.

(6) Abderhalden, *Z. physiol. Chem.*, **178** (1928), 253; ibid., **207** (1932), 141–146; ibid., **210** (1932), 246; *Biochem. Z.*, **211** (1929), 395; ibid., **226** (1930), 209.

conditions of the liquid silk. It will, therefore, lead to the different solubilities of sericin in water.

R. Inoue[7] measured already "kaijo" of cocoons by obtaining the curves of the amounts of nitrogen dissolved into the solution in a definite time. Further, he and T. Watanabe found that sericin on the outer layer of cocoons was more soluble in water than that on the inner layer. I confirmed fully their results and further found that the sericin solution obtained from cocoons having good "kaijo" or from the outer layer of cocoons had a stronger power of gelatinization and that this would lead to difficult conglomeration at the contact point of silk fiber on the cocoon.

When the cocoon layer containing the natural sericin is boiled with some distilled water in a flask with a reflux condenser, the sericin particles mostly disperse into the solution and form a hydro-philic colloid containing very small amounts of fatty and colouring matters.

The natural sericin is apt to denature to some extent by heat, alcohol, dialysis, and other external factors, so I used the sericin solution in that condition as the material to be examined. In general the solubility of sericin in water varies with the kinds of cocoons, with its total amounts existing on the cocoon fibers, with the amount of salts in water, and also with the temperature of the water.

The sericin is not a simple compound, but a mixture of similar proteins as described later. By the difference in the proportions of the mixtures in compliance with varieties of cocoons, the solubility in water will be affected, because each component has a different solubility in water.

The author determined some physico-chemical properties of aqueous solutions of the cocoon layer and observed that the solubility of sericin particles in dilute solutions is proportional to their relative viscosities, indices of refraction, or lowering of surface tension, and that the logarithm of solubility is also proportional to turbidity.

From these relations I was able to determine the solubility of sericin by measuring its physico-chemical properties. As already described, the solubility of sericin on the cocoon layer varies with its "kaijo." This will be caused mostly by the different proportions of two kinds of sericin, but it will also be affected by the different pH values of sericin solutions.

I have determined electrically the pH values of the sericin solutions, allowing them to stand for two hours after preparation. The results are shown in Table 1.

(7) R. Inoue, *Rep. Seric. and Silk Ind. Science*, **1** (1926), Vol. 1.

Table 1.

Cocoons having good "kaijo"		Cocoons having middle "kaijo"		Cocoons having bad "kaijo"	
conc. (%)	*p*H	conc. (%)	*p*H	conc. (%)	*p*H
0	4.88	—	—	—	—
0.05	4.96	0.07	5.09	0.07	4.92
0.09	5.70	0.10	5.29	0.11	5.09
0.11	5.79	0.14	5.38	0.14	5.30
0.16	5.89	0.16	5.81	0.16	5.62
0.20	5.96	0.19	5.86	0.24	5.73
0.26	6.01	0.22	5.97	0.29	5.78
0.35	6.21	0.31	6.05	0.38	5.98
0.40	6.20	0.42	6.11	0.48	6.08

Though the *p*H value of the sericin solution is a function of its concentration, a solution from cocoons having better "kaijo" shows the greater value in the same concentration. In order to clarify the cause of this difference of *p*H I made the following experiment.

A diaphragm with 0.1 g. cocoon layer was made at the middle point of an U-tube, 20 c.c. of distilled water free from carbon dioxide were poured into it, then the platinum electrodes were inserted at the ends of the tube, and an electric current of 110 volts was passed through. After an hour *p*H of each solution around the electrodes was measured.

The cathodic solution showed weak basicity (*p*H 7.43–7.81) and the anodic moderate acidity (*p*H 3.37–3.73). I detected qualitatively a minute amount of ammonia in the cathodic solution, and glycocoll, tyrosine, bitartrate. etc. in the anodic solution. It seemed to me that these compounds existed originally in the cocoon layer before the electric treatment and caused the change of *p*H.

Even for the same cocoon *p*H values of the solutions obtained by boiling it with water vary with the position of the layers.

The outer cocoon layer showed generally the greatest *p*H value, next the inner layer, and the middle layer the smallest, the difference in the values for these layers depending on "kaijo" of the cocoon. The swelling and the solubility of sericin increased greatly with the rise in temperature and two cases are expressed by the same equation.

$$W \times 100 = S = At^K \quad (A = 1.0),$$

where W represents the quantity of dissolved sericin in g. when 5 g. cocoons are boiled with 100 c.c. of distilled water in a flask for 30 minutes, t the temperature in centigrade, A and K constants.

The value of constant K depends not only on the temperature, but also on "kaijo" of the cocoon (Table 2).

Table 2.

"kaijo"	K(20–50°C.)	K(60–90°C.)	K(100°C.)
good	0.55	0.85	0.84
middle	0.43	0.71	0.77
bad	0.42	0.67	0.75

This leads to the conclusion that the sericin dispersed from the cocoon fibers having good "kaijo" contains more sericin A which is comparatively easily soluble even in cold water. And at the neighbourhood of 60°C. the solubility of sericin, that is constant K, increases rapidly.

2. **The Solubility of the Natural Sericin in Salt Solutions.** The neutral salts have generally a solvent action on proteins and under nearly all conditions exert a recognizable influence on proteins in solution. Denis (1856) noticed that the solubility of a certain protein increased by the addition of neutral salts and it is also known that in dilute solutions (less than 2 or 3 normal) neutral salts of the alkalies, or of alkali earth metals, increase the solubility of the protein in water. Cohen (1924) showed that the rate at which solubility is raised by increasing quantities of a salt is characteristic of each individual protein, and gave formula $S/S_0 = \alpha\mu^\beta$, where S_0 is the solubility of the protein in water, S the solubility in a salt solution with an ionic strength μ, α and β constants.

A. A. Green (1931)[8] also examined the solubility of hæmoglobin in salt solutions and showed that the solubility in concentrated solutions at constant pH and temperature was represented by an equation of the type:

$$\log S = \beta - K_s'\mu ,$$

where S is the solubility, μ the ionic strength, β an intercept constant which in the case of non-electrolytes is $\log S_0$, and K_s' the salting out con-

(8) A. A. Green, *J. Biol., Chem.*, **93** (1931), 495–541; ibid. **95** (1932), 47–66.

stant apparently independent of temperature and of pH but varying with salts. He obtained later the following experimental equation:

$$\log S - 1.6\sqrt{C} = 1.30 - k_0 C,$$

where C is the concentration of the salt and k_0 is a constant which varies with electrolytes.

The solubility of sericin on the cocoon in dilute salt solutions has been qualitatively investigated by R. Inoue[9] and he showed that the solubility of sericin increased in the presence of a small amount of salts (chlorides, sulphates, carbonates, etc.) and, on the contrary, decreased in concentrated salt solutions.

I also examined the solubility of sericin on the cocoon in salt solutions and obtained the following data: Cocoon layer 2.2 g. (Nichi 110 × Shi 103, 1931) were boiled with 100 c.c. of distilled water in a flask with a reflux condenser for 30 minutes, the solution was filtered, and then the solubility of sericin was estimated by the determination of nitrogen contained in the filtrate.

Log (S/S_0) is not proportional to the square root of concentration, $\sqrt{C}$, but it decreases gradually with increasing salt concentration.

$$\frac{\log (S/S_0)}{\sqrt{C}} + K_0 C = \text{const.} = K \quad \text{or} \quad \log (S/S_0) + K_0 C^{\frac{3}{2}} = K\sqrt{C},$$

where S is the solubility of sericin in pure water, K_0 and K constants.

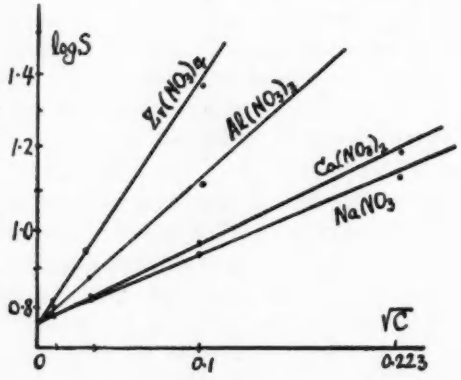

Fig. 1.

(9) R. Inoue, loc. cit.

The value of constant K depends on the nature of the cation of the inorganic salt, and it increases with increasing valency of the cation (Table 3 and Fig. 1).

Table 3

Nitrate	K	K_0	Chloride	K	K_0
$NaNO_3$	1.86	4	NaCl	1.85	10
$Ca(NO_3)_2$	2.11	4	$CaCl_2$	2.34	20
$Al(NO_3)_3$	6.00	50	$AlCl_3$	5.93	60
$Zr(NO_3)_4$	7.58	50	—	—	—

Solutions of sodium salts of organic acids

	K	K_0		K	K_0
Formate	1.74	2	Oleate	4.52	4
Acetate	1.75	2	Benzoate	1.65	2
Propionate	1.72	2	Benzene-sulphonate	1.60	2
Butyrate	1.715	2	Bitartrate	1.63	2
Valerate	1.706	2	Citrate	2.50	2

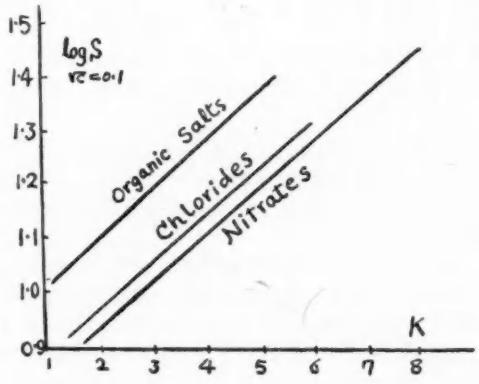

Fig. 2

The solubility of sericin increases in the presence of small amounts of nitrates, chlorides, or sodium salts of organic acids, and the relation

between the solubility and the concentration is expressed by the same equation:

$$\frac{\log \frac{S}{S_0}}{\sqrt{C}} + K_0 C = K.$$

At the same salt-concentration the values of constant K for salts used are proportional to the logarithm of the solubility of sericin as shown in Fig. 2. In the case of the sodium salts of lower fatty acids the solubility of sericin diminishes slightly with increasing number of carbon atoms in the molecule. The sodium salts of organic acids have stronger dispersing power for sericin than those of inorganic acids and the effect of anions of sodium salts on the solubility of sericin is reversed to the effect of anions on the solubility of fibroin (chloride<bitartrate<acetate<citrate).

Sec. II. The Relative Viscosity of Colloidal Solutions of Sericin.

There is one property in which hydrophilic colloids like sericin sol differ characteristically from water which acts as their dispersion medium. That is viscosity, and it is found that it increases with, but at a greater rate than, the concentration, showing that there is always some association.

For the measurement of the relative viscosity I used the well known Ostwald viscosimeter with a capillary tube of the inner diameter 0.08 cm.

The sericin sol was obtained by boiling about 5 g. of cocoon layers with 200 c.c. of distilled water in a flask with a reflux condenser for 30 minutes. After filtration it was immediately cooled to 20°C. in cold water, and then I measured its relative viscosity after leaving it to stand at 20°C. for 15 minutes.

(1) **Variation of Viscosity with Concentration.** The viscosities of sericin sols at varying concentrations are shown in Table 4. All these viscosities are expressed in the term of the viscosity of water at 20°C. which is taken as unity.

The slope of the viscosity-concentration curve as shown in Fig. 3 is an indication of the extent to which association between the solute and the solvent has occurred. The rise in viscosity with increasing concentrations is very rapid in solutions of sericin. The viscosity-concentration constant K or $\frac{\ln \eta^r}{C}$ is not strictly constant and increases gradually with increasing concentration of sericin and is given by the equation $K = aC + b$, where a and b are constants. But K can be considered to be constant in a narrow range of concentration.

Table 4

Relative Viscosity at 20°C., (good "kaijo").

Conc. C (g./100 c.c.)	flow. time t (sec.)	rela. visc. $\eta_r = \frac{td}{t_0 d_0}$	visc.—conc. const. $\frac{\ln \eta_r}{C} = K$
0.59	10.34	1.320	$0.2043 \times 2.3 = 0.4699$
0.47	9.74	1.233	0.1935 ,, = 0.4451
0.40	9.47	1.185	0.1843 ,, = 0.4239
0.38	9.40	1.171	0.1804 ,, = 0.4149
0.30	9.00	1.122	0.1666 ,, = 0.3832
0.28	9.05	1.115	0.1688 ,, = 0.3882
0.107	8.40	1.037	0.1474 ,, = 0.3380
0.00	8.12	1.000	—

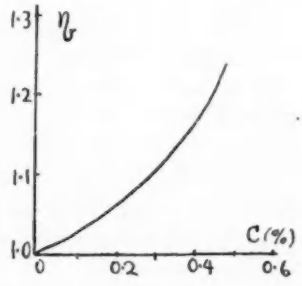

Fig. 3.

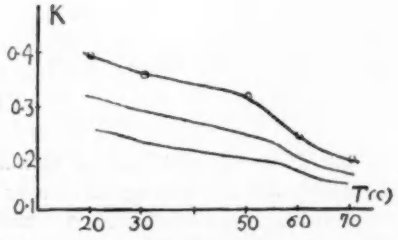

Fig. 4.

Sericin forms molecular aggregates in the aqueous solution and the value of the viscosity coefficient is a function of the volume of the molecular aggregates. For the polymeric organic materials Duclaux proposed the following equation:

$$M = \frac{\ln \eta_r}{C} \times 10^4 = K \times 10^4,$$

where M is the molecular weight of a polymeric material. Staudinger gave the following equation:

$$M = \frac{1}{K_{cm}} \cdot \frac{\ln \eta_r}{C} = \frac{K}{K_{cm}},$$

where K_{cm} is the molecular weight-concentration constant having a mean value 5×10^{-4}.

$$M = \frac{1}{5} K \times 10^4 \qquad (M > 50000)$$

If the equation of Duclaux holds also for sericin sol, its molecular weight would be 4026 in concentration of about 0.35 per cent. This molecular weight is ten times as great as the value calculated for the empirical formula $C_{15}H_{25}N_5O_8$ (= 403.0) of Bowmann.

Table 5.

	a	b	α	$M(C = 0.35\%)$
good "kaijo"	0.2711	0.310	0.0735	4026
middle ,,	0.2544	0.230	0.0647	3320
bad ,,	0.2075	0.161	0.0431	2382

$$\frac{\ln \eta_r}{C} = aC + b\,, \qquad \frac{\ln \eta_r}{C\left(C + \frac{b}{a}\right)} = a^2 = \alpha$$

It can be seen from Table 5 that the degree of aggregation of sericin particles obtained from a cocoon having good "kaijo" is greater than that of sericin micellæ obtained from a cocoon having bad "kaijo."

Though the calculated molecular weight depends on the diameter of capillary tube of the viscosimeter used, all correspond nearly to $403n$, where n may be any integer.

Staudinger considered that such an anomalous increase of viscosity would be due to the existence of long chain particles.

Fikentscher[10] recently proposed an equation containing a single arbitrary constant, which, although empirical, appears to be superior in general applicability to any hitherto used, namely

$$\frac{\ln \eta_r}{C} = \frac{ak^2}{1 + bkC} + k,$$

where C is the concentration in grams per 100 c.c. of the solution, a, b, and k constants, the last constant k being the arbitrary one, which

(10) H. Fikentscher and H. Mark, *Kolloid-Z.* **49** (1929), 135.

Fikentscher calls "Eigenviskosität." The values of constant k obtained from his equation for hydroxydecanoic acid polymeride are shown in Table 6.

Table 6.

mol. wt.	k	mol. wt.	k
780	0.020	9330	0.058
1710	0.025	16900	0.071
5670	0.042	20600	0.081

Table 7.

temp.	good "kaijo"			middle			bad		
(C.)	C	K	k_p	C	K	k_p	C	K	k_p
20	0.34	0.4025	0.067	0.34	0.3144	0.059	0.33	0.227	0.049
30	0.35	0.3536	0.063	0.34	0.2860	0.055	0.33	0.246	0.051
50	0.34	0.3200	0.060	0.33	0.239	0.051	0.32	0.211	0.044
60	0.34	0.2301	0.049	0.32	0.202	0.046	0.34	0.188	0.044
70	0.33	0.1925	0.045	0.35	0.1535	0.039	0.38	0.132	0.036

(k_p proper viscosity).

Both the viscosity-concentration constant K and proper viscosity k_p decrease with rising temperature (Table 7) and the value of $\frac{dK}{dt}$ changes suddenly near 60°C. as shown in Fig. 4. As already described sericin forms molecular aggregates in association with water molecules and this tendency to aggregate diminishes as temperature rises.

The value of K or k_p for sericin obtained from cocoons having good "kaijo" is always larger than that for sericin obtained from cocoons having bad "kaijo."

The sericin sol which has been obtained from cocoons having good "kaijo" and will have larger aggregation and higher hydration is more easily influenced by the temperature change. The solvation volumes of 1 g. sericin, b, calculated from Fikentscher's formula, are also a function of temperature (Table 8). B is the degree of solvation and is equal to b/v, where v is the specific volume.

Table 8.

temp.	good "kaijo"			middle			bad		
(C.)	*C*	*b*	*B*	*C*	*b*	*B*	*C*	*b*	*B*
20	0.34	16.2	21.22	0.34	12.6	16.44	0.33	8.1	10.53
30	0.34	14.0	18.34	0.35	12.1	15.79	0.32	8.5	11.05
50	0.36	13.4	—	0.36	9.2	—	0.36	7.1	—
60	0.33	8.2	—	0.36	8.5	—	0.36	7.7	—
70	0.32	6.5	—	0.33	5.2	—	0.33	4.1	—

It can be presumed that above 60°C. the sol form of sericin is present, while below 20°C. the gel form occurs. Between these temperatures both forms will be present in a ratio depending on the temperature and the age of the solution. Hardy considered that the ionized protein had a greater effect on the viscosity of water than the unionized, and, with Pauli and Samec (1909), he attributed this to a greater association between the ionized protein and water.

2. **Variation of Viscosity with Time.** The viscosity of the sericin solutions in which the formation of colloidal micellæ occurs is not constant, but changes with time, showing there is a gradual change in structure. The increase of viscosity of sericin solutions with time, which ultimately leads to gelatinization, is probably due to separation of finely dispersed precipitate throughout the system.

The effect of time on viscosity is the greatest between 20° and 60°C.. Below 20°C., or above 50°C., the variation of viscosity with time is very small for a few hours (Table 9).

Table 9.

time	0°C.	10°C.	20°C.	50°C.	70°C.
(min.)	0.35 %	0.32 %	0.32 %	0.27 %	0.43 %
15	22.21	12.35	9.07	5.94	5.98
30	21.93	12.30	9.36	6.09	6.04
45	21.73	12.50	9.45	6.30	6.17
60	21.64	12.43	9.47	6.66	6.20
120	22.50	12.45	9 50	8.96	6.17
180	22.89	12.50	9.28	9.80	6.23

Above 60°C. the curve runs practically parallel to the time axis; at lower temperatures, an increase in viscosity with the time is clearly noticed. (Fig. 5).

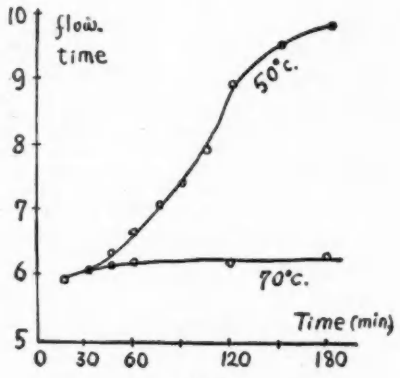

Fig. 5.

3. Variation of Viscosity with Time and Temperature.

In making a solution of sericin by heating cocoons in distilled water, the sericin dissolved entirely in sol form, which was cooled immediately, and viscosity measurements were made after 15 minutes.

The logarithm of flowing time in sec. of sericin solutions is a linear function of the logarithm of temperatures in centigrade; $\ln t = \ln \alpha - \beta \ln T$ or $t = \alpha T^{-\beta}$, where α and β are constants (Table 10).

Table 10.

"kaijo"	α	β	conc.
good	14.1	0.20	0.45%
middle	12.2	0.18	0.26%
bad	12.2	0.18	0.28%

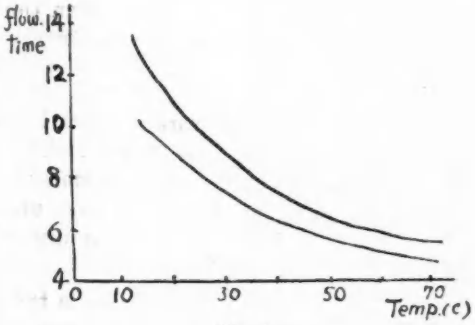

Fig. 6.

Constant α depends on the concentration of the sericin solution and constant β on the aggregation of sericin particles.

4. Effect of Acids and Alkalis on the Viscosity. The condition in which sericin dissolves has a considerable effect on the viscosity of the solution. At the isoelectric point the charge of sericin particles is zero, and, since the electro-viscous effect is necessarily minimum at this point, the viscosity must increase both with an increase and with a decrease of the hydrogen-ion exponent.

The relation between the viscosity and hydrogen-ion concentration are shown in Table 11.

Table 11.

Effect of HCl, (at 20°C.).

good (0.185 %)		mid. (0.20%)		bad (0.175 %)	
flow. time	*p*H	flow. time	*p*H	flow. time	*p*H
8.65	4.665	8.50	4.50	8.29	4.40
8.55	4.060	8.44	4.26	8.21	4.29
8.52	4.025	8.31	4.18	8.20	4.25
8.50	3.985	8.26	4.12	8.16	4.175
8.31	3.960	8.25	4.00	8.31	3.73
8.62	3.520	8.51	3.58	8.34	3.68
8.75	2.810	8.68	2.78	8.50	2.77
8.82	2.450	8.73	2.37	8.58	2.27

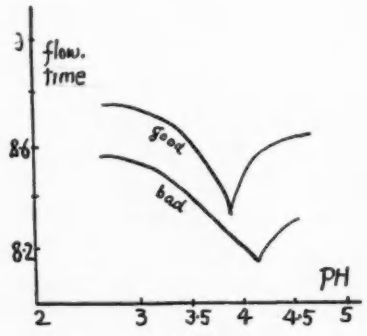

Fig. 7.

The influence of hydrogen-ion concentration on the viscosity of sericin is reproduced in Fig. 7. As shown in Table 11 the *p*H value has a much marked effect on the viscosity, the viscosity coefficient for 0.2 per cent. solution of sericin rising from 8.5 at *p*H 4.0 to 8.82 at *p*H 2.45. The point of minimum viscosity in sericin coincides with the isoelectric point.

For sericin sol the hydrogen-ion concentration of the isoelectric point varies with the concentration of the protein (Table 12).

Table 12.

Isoelectric point of sericin.

"kaijo"	0.2 %	0.12 %
good	3.95	3.80
middle	4.12	3.97
bad	4.18	4.08

Table 13.

vol. added in c.c.	0.1*N* NaOH 0.22 %	0.1*N* NH_4OH 0.29 %
0	1.080	1.110
0.05	1.130	1.130
0.1	1.105	1.183
0.2	1.085	1.210
0.3	1.071	1.225

The isoelectric point of sericin obtained from cocoons having good "kaijo" is always more acidic than that of sericin obtained from cocoons having bad "kaijo." The viscosity of sericin in alkaline solution increases with the concentration of alkali and attains to the maximum point and falls again with increased hydroxyl-ion activity (Table 13).

5. Effect of Inorganic Salts on the Viscosity. I investigated the effect of inorganic salts which are commonly contained in small amounts in the natural water on the viscosity of the sericin solution (Table 14).

Table 14.

(10 c.c. sericin solution + x c.c. salt solution + (2–x)c.c. water).

$\frac{N}{100}$ salt solution added in c.c. x	0.08 per cent. sericin solution (at 20°C), flowing time in sec.				
	NaCl	KNO_3	$MgCl_2$	$CaCl_2$	$FeCl_3$
0	9.7	9.7	9.7	9.7	9.7
0.1	9.8	9.2	10.2	10.4	10.0
0.3	9.8	9.3	10.8	10.5	10.2
0.5	10.1	9.6	11.2	10.8	10.6
0.7	10.4	10.0	11.6	10.6	11.0
0.9	10.8	10.2	11.8	10.4	10.9
1.1	10.9	10.5	12.2	10.3	10.6
1.5	12.0	10.7	13.5	10.2	10.6

When potassium nitrate is added to a sericin solution there is first a decrease in the viscosity. When more of the salt is added the viscosity continually increases. In the case of calcium chloride and ferric chloride the effect on the viscosity is contrary to the case of potassium nitrate. The viscosity, after passing through a maximum, goes on decreasing. When sodium chloride or magnesium chloride is added to the same solution the viscosity increases with increasing concentration of the electrolyte (Fig. 8).

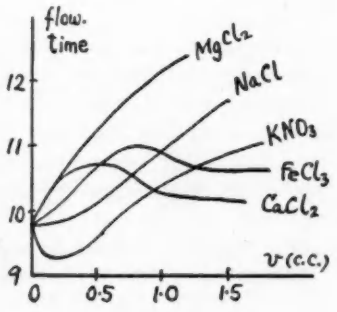

Fig. 8.

SUR L'ÉQUILIBRE HÉTÉROGÈNE DU SYSTÈME TERNAIRE DES COMPOSÉS ORGANIQUES.

Par Tei-ichi ASAHINA.

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Une méthode simple d'analyse thermique a été proposées, il y a une dizaine d'années, par M. H. Rheinboldt,[1] et a trouvé généralement son usage dans l'étude des composés moléculaires organiques surtout réalisée par cet auteur, par M. P. Pfeiffer et par leurs élèves.[1] Nous l'avons aussi utilisée et elle nous a donné de bons résultats.[2] Elle n'a le plus souvent été appliquée jusqu'ici qu'aux systèmes binaires, mais on peut raisonnablement l'appliquer aux systèmes ternaires des composés organiques et, généralement, à tous les composés dont les points de fusion sont relativement bas. Cette application a été tentée et nous a donné de bons résultats que nous rapportons ci-dessous. Un des buts de cette étude est la recherche de composés moléculaires ternaires nouveaux. Comme exemple de cette tentative, le système: β-naphthol, méthylènedioxybenzal-acétophénone et acide picrique a été étudié. On savait déjà qu'il y a formation de composés moléculaires entre la méthylènedioxybenzal-acétophénone et l'acide picrique (le rapport moléculaire étant 1:2)[3] et aussi entre le β-naphthol et l'acide picrique (la proportion moléculaire étant 1:1)[4] mais cette formation n'avait jamais été obervée entre le β-naphthol et la chalcone.[3]

Premièrement nous avons fait les trois diagrammes d'équilibre hétérogène correspondants aux trois systèmes binaires. (Voyez les tables 1–3 et les figures 1–3). Ensuite nous avons préparé plusieurs mélanges d'acide picrique et de naphthol en diverses proportions et nous avons cherché l'état d'équilibre entre chacun d'eux et la chalcone, les températures de dégel et de congel étant données dans les tables 4-12 et les figures 4-12.

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(1) P. Pfeiffer "Organische Molekülverbindungen," 1927, 66–85.

(2) *Acta Phytochimica*, **7** (1933), 187; Ce bulletin, **9** (1934), 131 et 181.

(3) Ce bulletin, **9** (1934), 131.

(4) Ce système a été étudié par M. B. Kuriloff, les compositions des mélanges étant exprimées en mol-pourcentages. Nous avons répéte l'expérimentation d'après notre méthode et nous avons trouvé qu'il y a un peu de discordance entre ses données et les nôtres. Voyez *Z. physik. Chem.*, **23** (1897), 673; **24** (1897), 441; et aussi C. Marchetti; *Gazz. chim. ital.*, **12** (1882), 503.

Table 1. (Voyez la Fig. 1.)

constituants du système				températures	
acide picrique		β-naphthol		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.	—	100.0	—	—	121.5
10.0	0.0300	90.0	0.2700	109.0	117.0
20.0	0.0400	80.0	0.1600	109.2	115.2
30.0	0.0600	70.0	0.1400	109.3	133.5
40.0	0.0800	60.0	0.1200	108.0	145.5
50.0	0.1200	50.0	0.1200	111.0	153.0
60.0	0.1659	40.0	0.1106	135.0	156.3
70.0	0.1400	30.0	0.0600	109.5	154.0
80.0	0.1600	20.0	0.0400	109.2	142.5
90.0	0.1800	10.0	0.0200	109.0	121.5
100.0	—	0.0	—	—	122.0

Table 1a. (d'après M. Kuriloff.)

constituants du système				mol. % d' acide picrique	points de fusion
acide picrique		β-naphthol			
%	g.	%	g.		°C.
0	—	100.0	—	0	121.0
7.5	0.0916	92.5	1.1266	4.87	117.0
18.4	0.3714	81.6	1.6494	12.4	127.0
32.4	0.4978	67.6	1.0387	23.1	136.4
46.4	0.5106	53.6	0.5914	35.2	150.8
61.3	2.2615	38.7	1.4267	49.9	157.0
61.3	0.8675	38.7	0.5449	50.0	157.0
62.6	0.7330	37.4	0.4363	51.4	156.4
72.8	3.1089	27.2	1.1634	62.9	151.0
78.8	2.2878	21.2	0.6158	70.2	146.0
90.3	2.3769	9.7	0.2552	85.4	120.2
90.9	3.1089	9.1	0.3095	86.4	118.0
97.2	2.2296	2.8	0.0647	95.6	117.0
100.0	—*	0.0	—*	100. *	122.2

*Les chiffres des ces colonnes sont ceux qui ont été donnés en pourcentages moléculaires par M. Kuriloff. Nous les donnons dans les première et troisième colonnes convertis en pourcentages en poids.

Table 2. (Voyez la Fig. 2.)

constituants du système				tempèratures	
méthylènedioxychalcone		β-naphthol		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.5
10.4	0.0021	89.6	0.0180	72.0	116.5
20.0	0.0040	80.0	0.0160	72.0	111.5
30.0	0.0060	70.0	0.0140	71.0	104.5
40.0	0.0080	60.0	0.0120	72.0	95.5
50.0	0.0100	50.0	0.0100	71.0	83.8
60.0	0.0120	40.0	0.0080	71.0	80.0
70.0	0.0140	30.0	0.0060	71.0	95.5
75.0	0.0150	25.0	0.0050	71.5	100.5
80.0	0.0160	20.0	0.0040	71.0	106.6
85.0	0.0170	15.0	0.0030	72.0	110.8
90.0	0.0180	10.0	0.0020	71.5	114.5
95.0	0.0190	5.0	0.0010	72.0	118.4
100.0	—	0.0	—	—	121.0

Table 3. (Voyez la Fig. 3.)

constituants du système				températures	
méthylènedioxychalcone		acide picrique		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	122.0
2.7	0.0011	97.3	0.0400	113.5	120.0
4.8	0.0010	95.2	0.0200	113.5	116.5
10.0	0.0010	90.0	0.0090	113.5	119.8
14.2	0.0010	85.8	0.0060	113.5	123.0
21.3	0.0016	78.7	0.0059	113.5	126.5
24.7	0.0020	75.3	0.0061	113.5	127.2
25.0	0.0050	75.0	0.0150	113.0	127.3
34.1	0.0030	65.9	0.0058	114.5	128.5
40.6	0.0041	59.4	0.0060	104.5	128.0
52.6	0.0050	47.4	0.0045	105.0	125.3
64.1	0.0066	35.9	0.0037	104.0	117.5
70.0	0.0140	30.0	0.0060	104.0	111.0
80.0	0.0160	20.0	0.0040	104.3	110.0
85.0	0.0170	15.0	0.0030	103.5	113.5
90.0	0.0180	10.0	0.0020	104.0	116.5
95.0	0.0190	5.0	0.0010	104.5	119.0
100.0	—	0.0	—	—	121.0

Table 4. (Voyez la Fig. 4.)

constituants du système				températures	
acide picrique 10% + β-naphthol 90%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
4.0	0.0006	96.0	0.0144	92.1	118.5
20.0	0.0030	80.0	0.0120	68.3	106.5
26.8	0.0044	73.2	0.0120	67.0	99.0
38.0	0.0057	62.0	0.0093	69.0	85.5
50.0	0.0065	50.0	0.0065	70.0	75.5
65.0	0.0130	35.0	0.0070	69.5	94.2
79.0	0.0120	21.0	0.0032	69.8	106.0
88.8	0.0135	11.2	0.0017	71.0	112.3
100.0	—	0.0	—	109.0	117.0

Table 5. (Voyez la Fig. 5.)

constituants du système				températures	
acide picrique 20% + β-naphthol 80%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	68.0	114.5
20.0	0.0030	80.0	0.0120	68.0	106.5
30.0	0.0045	70.0	0.0105	67.0	97.0
44.0	0.0066	56.0	0.0084	67.5	82.5
50.0	0.0070	50.0	0.0070	70.0	79.0
60.0	0.0090	40.0	0.0060	68.5	94.0
80.0	0.0120	20.0	0.0030	70.0	110.0
100.0	—	0.0	—	109.2	115.2

Table 6. (Voyez la Fig. 6.)

constituants du système				températures	
acide picrique 30% + β-naphthol 70%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	68.0	116.2
20.0	0.0030	80.0	0.0120	70.0	108.0
34.0	0.0051	66.0	0.0099	70.0	95.0
42.0	0.0063	58.0	0.0087	69.0	85.0
54.0	0.0081	46.0	0.0069	70.0	99.0
60.0	0.0090	40.0	0.0060	69.5	107.0
70.0	0.0105	30.0	0.0045	70.0	118.5
84.0	0.0126	16.0	0.0024	70.0	127.0
100.0	—	0.0	—	109.3	133.5

Table 7. (Voyez la Fig. 7.)

constituants du système				températures	
acide picrique 40% + β-naphthol 60%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	69.8	115.3
20.0	0.0030	80.0	0.0120	70.0	108.2
30.0	0.0045	70.0	0.0105	70.0	100.0
40.0	0.0040	60.0	0.0060	69.5	91.0
50.0	0.0070	50.0	0.0070	70.0	102.0
70.0	0.0105	30.0	0.0045	69.5	127.0
80.0	0.0120	20.0	0.0030	70.0	136.0
90.0	0.0135	10.0	0.0015	70.0	142.2
100.0	—	0.0	—	108.0	145.5

Table 8. (Voyez la Fig. 8.)

constituants du système				températures	
acide picrique 50% + β-naphthol 50%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	73.0	115.5
20.0	0.0030	80.0	0.0120	70.5	110.0
30.0	0.0045	70.0	0.0105	70.0	100.5
40.0	0.0080	60.0	0.0120	70.0	91.2
50.0	0.0060	50.0	0.0060	68.5	104.5
60.0	0.0090	40.0	0.0060	69.0	120.5
70.0	0.0105	30.0	0.0045	69.0	133.0
79·5	0.0120	20.5	0.0031	69.0	140.0
90.0	0.0135	10.0	0.0015	69.5	148.0
100.0	—	0.0	—	111.0	153.0

Table 9. (Voyez la Fig. 9.)

constituants du système				températures	
acide picrique 60% + β-naphthol 40%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	85.5	115.5
20.0	0.0030	80.0	0.0120	84.5	109.3
30.0	0.0045	70.0	0.0105	84.0	102.0
40.0	0.0060	60.0	0.0090	84.5	93.2
50.0	0.0105	50.0	0.0105	85.0	105.5
60.0	0.0090	40.0	0.0060	84.0	119.5
70.0	0.0105	30.0	0.0045	84.0	132.0
80.0	0.0120	20.0	0.0030	84.0	139.0
90.0	0.0135	10.0	0.0015	81.5	149.0
100.0	—	0.0	—	135.0	156.3

Table 10. (Voyez la Fig. 10.)

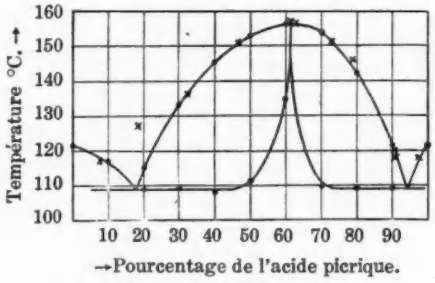
cconstituants du système				températures	
acide picrique 70% + β-naphthol 30%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	85.0	117.0
20.0	0.0030	80.0	0.0120	85.0	110.0
30.0	0.0045	70.0	0.0105	84.0	105.1
40.0	0.0060	60.0	0.0090	82.0	101.0
50.0	0.0070	50.0	0.0070	84.1	106.0
59.2	0.0090	40.8	0.0062	84.0	114.5
70.0	0.0105	30.0	0.0045	84.3	127.5
77.9	0.0120	22.1	0.0034	83.0	135.2
90.0	0.0135	10.0	0.0015	102.5	144.0
100.0	—	0.0	—	109.5	154.0

Table 11. (Voyez la Fig. 11.)

constituants du système				températures	
acide picrique 80% + β-naphthol 20%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0 0135	86.0	117.0
20.0	0.0030	80.0	0.0120	85.0	110.0
30.0	0.0045	70.0	0.0105	83.0	104.0
40.0	0.0060	60.0	0.0090	84.5	108.0
50.0	0.0070	50.0	0.0070	83.5	114 0
59.6	0.0090	40.4	0.0061	85.2	116.0
69.5	0.0105	30.5	0.0046	84.5	116.0
79.5	0.0120	20.5	0.0031	101.5	126.0
90.0	0.0135	10.0	0.0015	101.5	134.0
100.0	—	0.0	—	109.2	142.5

Table 12. (Voyez la Fig. 12.)

constituants du système				températures	
acide picrique 90% + β-naphthol 10%		méthylènedioxy-chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	83.0	117.0
20.0	0.0030	80.0	0.0120	83.0	110.0
30.0	0.0045	70.0	0.0105	84.5	106.0
40.0	0.0060	60.0	0.0090	83.0	114.0
50.0	0.0070	50.0	0.0070	82.0	120.0
60.0	0.0090	40.0	0.0060	84.0	123.0
70.0	0.0105	30.0	0.0045	102.0	122.2
79.5	0.0120	20.5	0.0031	102.0	119.5
89.4	0.0135	10.6	0.0016	104.5	113.5
96.0	0.0144	4.0	0.0006	102.0	117.0
100.0	—	0.0	—	109.0	121.5

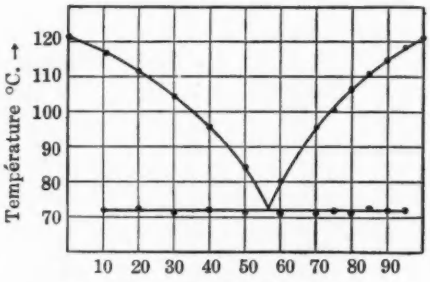


→Pourcentage de l'acide picrique.

• ..... d'après le present auteur.

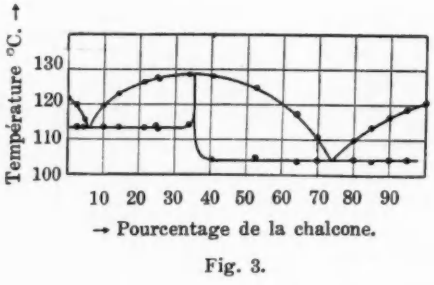
× ..... d'après M. Kuriloff.

Fig. 1.



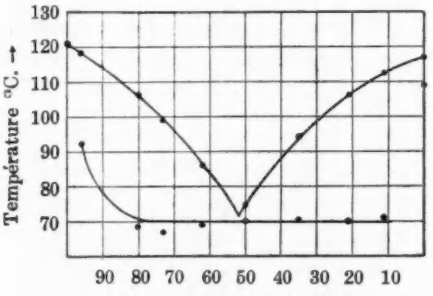
→Pourcentage de la chalcone.

Fig. 2.



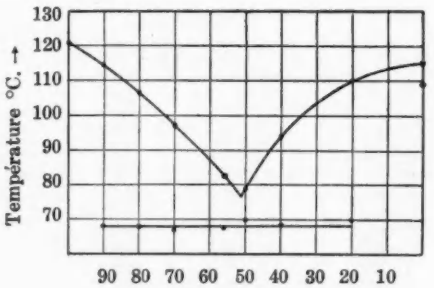
→ Pourcentage de la chalcone.

Fig. 3.



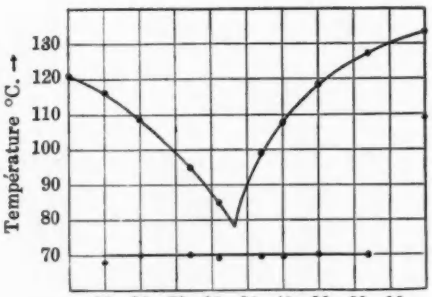
← Pourcentage de la chalcone.

Fig. 4.



← Pourcentage de la chalcone.

Fig. 5.



← Pourcentage de la chalcone.

Fig. 6.

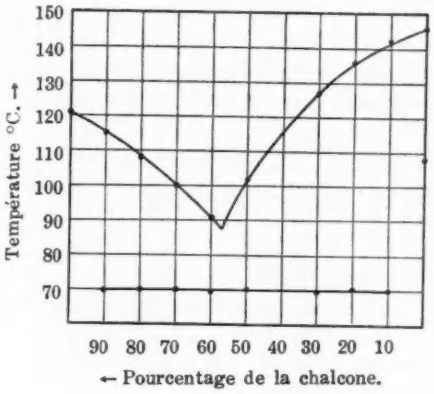


Fig. 7.

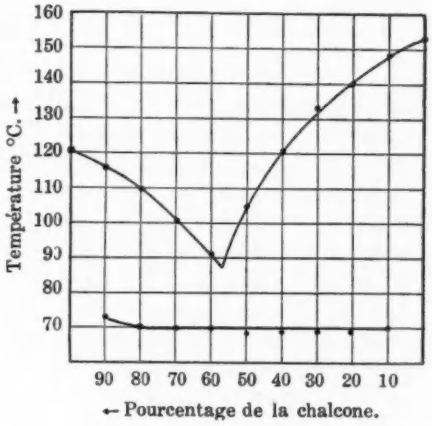


Fig. 8.

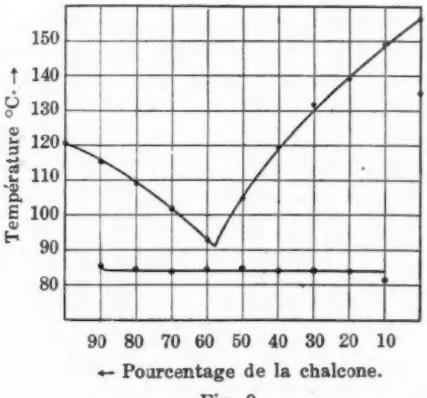


Fig. 9.

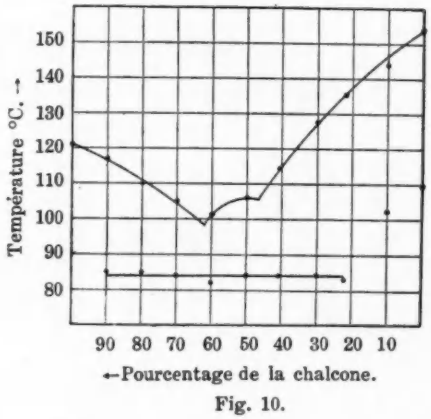


Fig. 10.

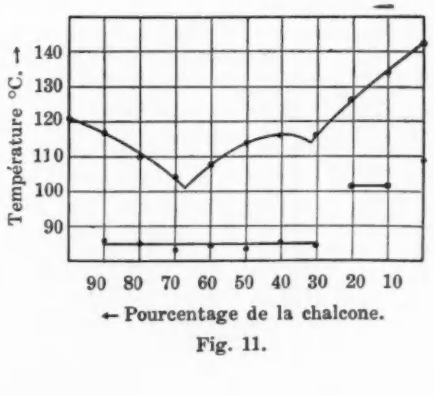


Fig. 11.

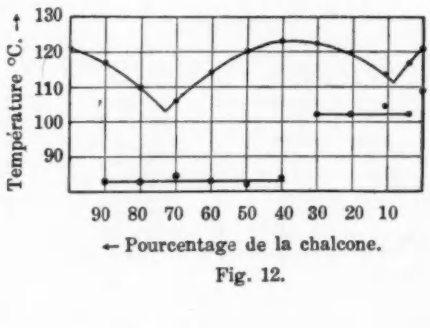


Fig. 12.

Par interpolation dans les 12 diagrammes, on peut trouver le pourcentage correspondant à chaque point de congel. On peut ainsi faire des isothermes de cinq en cinq degrés et obtenir un diagramme d'équilibre hétérogène du système ternaire. (Fig. 21.)

Toutefois, pour les réaliser complètement, il a fallu préciser leur valeur dans le domaine voisin de 100% d'acide picrique. On a fait quelques mesures additionnelles qui sont indiquées ci-dessous. (Voyez les tables 13–19 et les figures 13–19). Dans la figure 20, on donne les lignes, le long desquelles toutes les observations mentionnées ont été rapportées. La figure 21 est le diagramme complète d'équilibre hétérogène des phases solides et liquides du système ternaire. Il montre clairement d'une part qu'il n'y a pas de formation de composé moléculaire, et d'autre part que ce système ternaire presente trois points eutectiques.

Table 13. (Voyez la Fig. 13.)

constituants du système				températures	
acide picrique 90%+ méthylènedioxychalcone 10%		acide picrique 90%+ β-naphthol 10%		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
20.0	0.0030	80.0	0.0120	102.5	113.0
30.0	0.0030	70.0	0.0070	102.0	111.0
40.0	0.0060	60.0	0.0090	103.0	110.5
50.0	0.0050	50.0	0.0050	103.0	112.0
60.0	0.0090	40.0	0.0060	102.5	112.0
70.0	0.0070	30.0	0.0030	102.5	113.0
79.0	0.0120	21.0	0.0032	102.5	113.0
100.0	—	0.0	—	113.5	119.8

Table 14. (Voyez la Fig. 14.)

Le mélange de méthylènedioxychalcone 20% et β-naphthol 80% . . . . . A.
Le mélange de méthylènedioxychalcone 20% et acide picrique 80% . . . . B.

A	B	A : B	températures	
			points de dégel	points de congel
g.	g.		°C.	°C.
sans le B	—	—	72.0	111.5
0.0140	0.0020	7 : 1	68.0	105.0
0.0120	0.0040	6 : 2	70.0	117.0
0.0100	0.0060	5 : 3	68.0	130.0
0.0080	0.0080	4 : 4	69.0	139.0
0.0060	0.0100	3 : 5	89.0	139.5
0.0040	0.0120	2 : 6	102.5	130.0
0.0020	0.0140	1 : 7	104.0	117.0
—	sans l'A		113.5	125.7

Table 15. (Voyez la Fig. 15.)

Le mélange de méthylènedioxychalcone 40% et β-naphthol 60% ..... A.
Le mélange de méthylènedioxychalcone 40% et acide picrique 60% .... B.

A	B	A : B	températures	
			points de dégel	point de congel
g.	g.		°C.	°C.
sans le B	—		72.0	95.5
0.0110	0.0010	5.5 : 0.5	69.5	90.0
0.0100	0.0020	5 : 1	70.0	91.0
0.0100	0.0050	4 : 2	70.0	109.0
0.0080	0.0080	3 : 3	69.0	120.5
0.0040	0.0080	2 : 4	88.2	117.0
0.0020	0.0100	1 : 5	87.0	120.5
0.0010	0.0110	0.5 : 5.5	87.0	124.5
—	sans l'A		104.5	128.3

Table 16. (Voyez la Fig. 16.)

Le mélange d'acide picrique 70% et β-naphthol 30% ..... A.
Le mélange d'acide picrique 70% et méthylènedioxychalcone 30% ..... B.

A	B	A : B	températures	
			points de dégel	points de congel
g.	g.		°C.	°C.
sans le B	—		109.5	154.0
0.0500	0.0100	5 : 1	102.3	147.0
0.0500	0.0250	4 : 2	103.0	136.5
0.0600	0.0600	3 : 3	102.2	126.0
0.0300	0.0600	2 : 4	103.0	116.2
0.0100	0.0500	1 : 5	103.5	124.0
—	sans l'A		113.7	129.0

Dans les trois tables 17—19, on met
le mélange d'acide picrique 70%+β-naphthol 30% ..... *X*.
le mélange d'acide picrique 70%+méthylènedioxychalcone 30% ..... *Y*.

Table 17. (Voyez la Fig. 17.)

Le mélange de $X : Y = 4 : 2$ ..... A.
Acide picrique ..... B.

A	B	A : B	températures	
			points de dégel	points de congel
g.	g.		°C.	°C.
sans le B	—		103.0	136.5
0.0100	0.0020	5 : 1	103.0	133.0
0.0080	0.0040	4 : 2	103.3	127.0
0.0060	0.0060	3 : 3	103.5	118.2
0.0040	0.0080	2 : 4	103.5	111.0
0.0020	0.0100	1 : 5	103.2	117.5
—	sans l'A			122.0

Table 18. (Voyez la Fig. 18.)

Le mélange de $X : Y = 3 : 3$ ..... A.
Acide picrique ..... B.

A	B	A : B	températures	
			points de dégel	points de congel
g.	g.		°C.	°C.
sans le B	—		102.2	126.0
0.0100	0.0020	5 : 1	103.0	123.0
0.0080	0.0040	4 : 2	103.0	116.0
0.0060	0.0060	3 : 3	103.0	108.5
0.0040	0.0080	2 : 4	103.0	111.5
0.0020	0.0100	1 : 5	102.5	117.0
—	sans l'A			122.0

Table 19. (Voyez la Fig. 19.)

Le mélange de $X : Y = 2 : 4$ ..... A.
Acide picrique ..... B.

A	B	A : B	températures	
			points de dégel	points de congel
g.	g.		°C.	°C.
sans le B	—		103.0	116.2
0.0100	0.0020	5 : 1	103.0	116.0
0.0100	0.0050	4 : 2	103.2	115.5
0.0060	0.0060	3 : 3	103.2	113.0
0.0040	0.0080	2 : 4	103.0	113.0
0.0020	0.0100	1 : 5	103.0	117.5
—	sans l'A			122.0

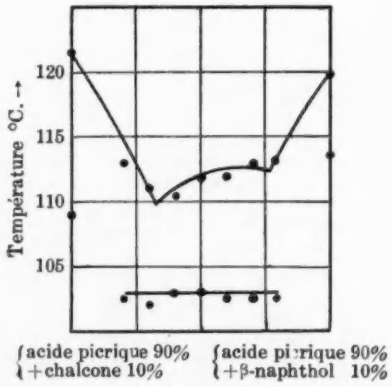


Fig. 13.

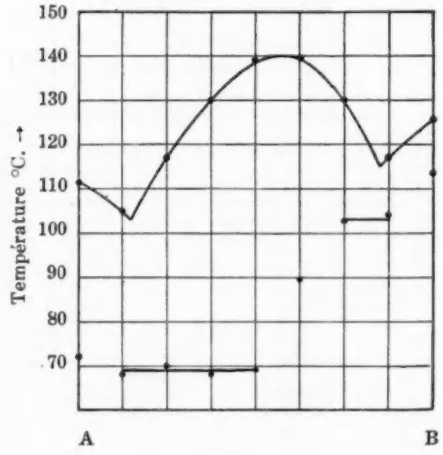


Fig. 14.

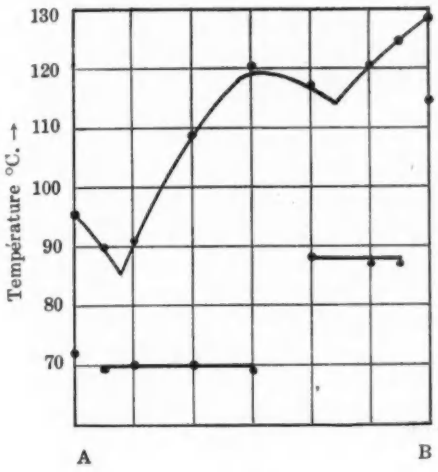


Fig. 15.

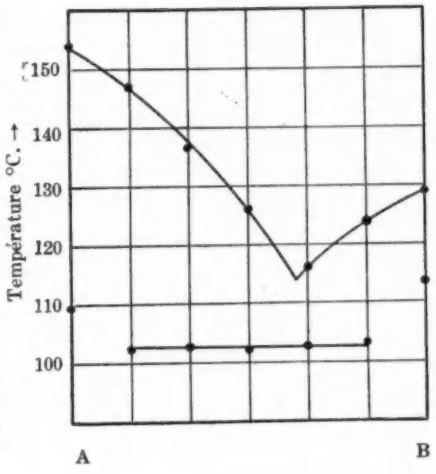


Fig. 16.

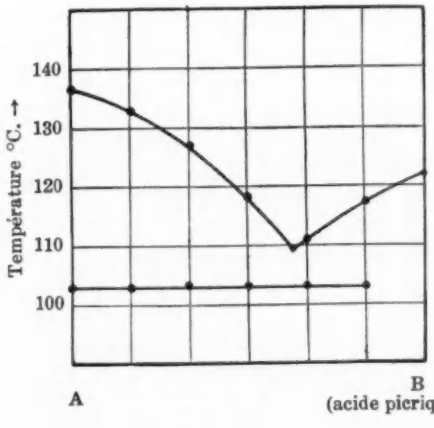


Fig. 17.

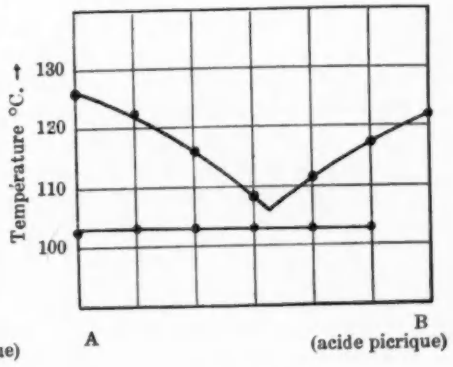


Fig. 18.

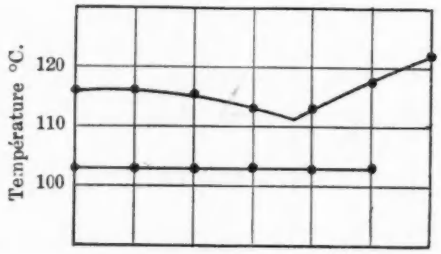
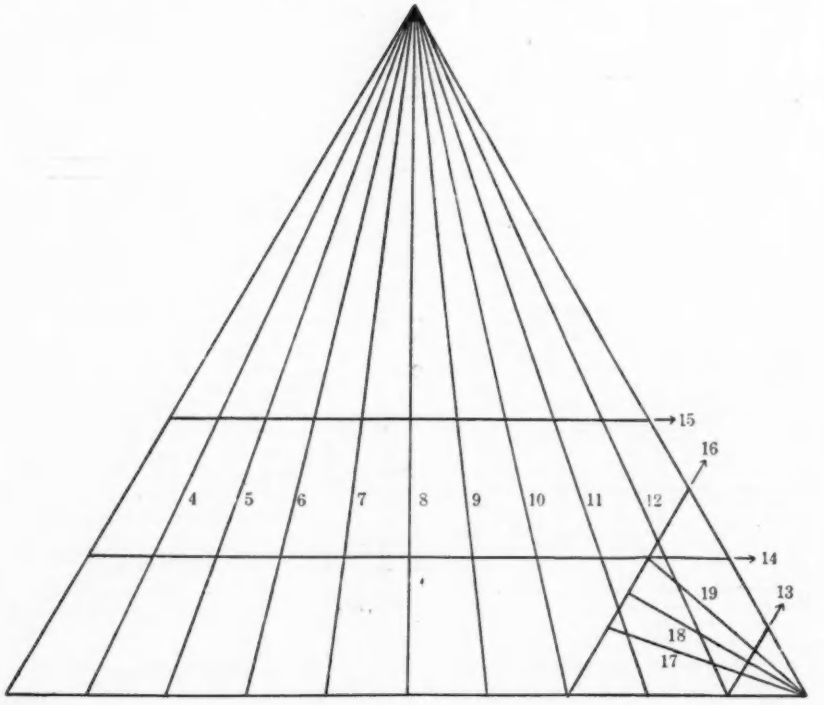


Fig. 19

Méthylènedioxychalcone.

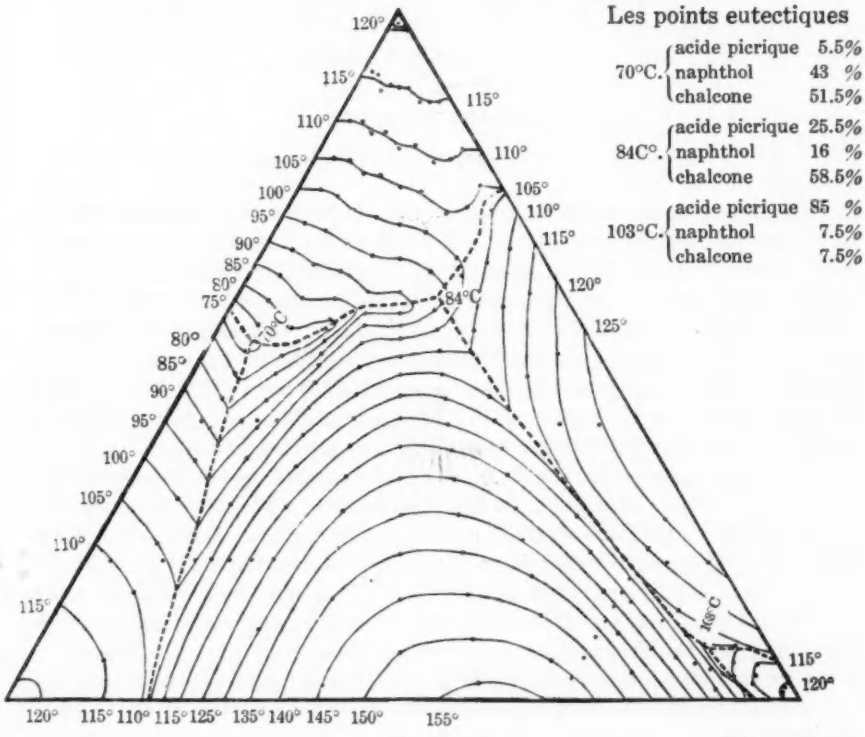


β-Naphthol. Acide picrique.

Les chiffres sont identiques aux nombres des figures 4—19.

Fig. 20. see errata V. 9, P. 558

Méthylènedioxychalcone.



β-Naphthol. Fig. 21. Acide picrique.

En terminant l'auteur tient à remercier a M. K. Yokoyama, aide privé, qui l'a assisté dans ses experiences et à M. le prof. Y. Shibata pour les conseils qu'il lui a prodigués.

Le Dr. Motte de la Maison franco-japonaise de Tokio, a eu la bontè de revoir ce mémoire au point de vue linguistique : nous l'en remercions sincèrement ici.

Laboratoire de Chimie, Faculté des Sciences,
Université Impériale de Tokio.

RHYTHMIC PRECIPITATES. III. ON THE EFFECTS OF THE PRESENCE OF ACIDS, ALCOHOLS, OR AMINO-ACIDS IN GELATINE JELLIES.

By Toshizo ISEMURA.

Received April 28th, 1934. Published May 28th, 1934.

In the previous communication,[1] the author reported the effects on the rhythmic precipitates of light and the aging of gel before the superposition of the diffusing electrolyte on it. In the present paper the experimental results are described on the effects of the presence of some fatty acids, alcohols, and amino-acids in the gelatine jellies. It is a known fact that the addition of a small quantity of a capillarily active material such as fatty acids or alcohols decreases the surface tension of water, while the addition of some amino-acids increases it. It may be interesting, therefore, to study the effects of these substances on the bands of rhythmic precipitates.

Ordinary rhythmic precipitates of silver chromate in gelatine jelly have been tested, It is desirable, in the present experiment, that impurities contained in the gelatine should be as little as possible. Powdered "Gelatine white" from Merck has been dialyzed for about five days in distilled water. In this dialyzed gelatine the secondary rhythmic precipitates in gelatine-silver chromate system has no more been observed which were pointed out as the chloride and phosphate of silver.[2]

The gel was prepared by mixing equal volumes of the sol containing 0.2 per cent. potassium dichromate and the aqueous solution of the acid or alcohol. After 24 hours the 20 per cent. silver nitrate solution was superposed on the gel. Caution was taken so that in one series of experiments the sol used in preparing the jelly should be the same and the test-tubes should be of possibly equal diameters. Moreover, the heights of the jelly and the upper electrolyte in each test-tube were made as equal as possible.

The Effect of Fatty Acids. According to Traube's rule, the larger the molecular weight of the fatty acid in water is, the greater the decrease of surface tension of water is, provided the concentrations of the acid being the same. Propionic, butyric, capronic, and caprylic acids have been tested, and the gelatine jelly containing 0.05 mol. of the fatty acid per litre has been used. The results of the experiments are as follows:

(1) Isemura, this Bulletin, **8** (1933), 108.

(2) Hedge, "Liesegang Rings," (1932), 23. Riegel and Reihard, *J. Phys. Chem.*, **31** (1927), 713. Schleussner, *Kolloid-Z.*, **31** (1922), 347; **34** (1924), 338.

No acid: well-known rhythmic precipitates were observed.
Propionic acid: no band or a few faint bands were observed.
Butyric acid: no band or a few faint bands were observed.
Capronic acid: a few bands consisting of large crystals were observed.
Caprylic acid: two kinds of bands were recognized.

In the cases of propionic and butyric acids, bands did not appear in general. Under certain circumstances, however, a few bands have been observed near the contact surface with the upper electrolyte. In the case of capronic acid, several bands were observed, each of which was composed of considerably large crystals. This was caused, probably, by the deposition of silver chromate crystals on the initially formed bands of the silver soap. At first, white silver capronate in small granules deposits into bands, which then are coated gradually with brick-red silver chromate. The same process has been recognized much more distinctly in the case of caprylic acid. The solubility of caprylic acid in water is small, and the solution containing 0.05 mol. per litre is not homogeneous, but forms an emulsion. In this case, first the long orange layer of silver chromate deposited and in this layer the banding of comparatively large crystals were observed, which is considered silver caprylate. In the lower part of the test tube banding of white granules appeared, which then changed into brick-red in colour in the course of time. It is conceived that the granules of silver caprylate were coated with silver chromate.

In general, the addition of the fatty acid to the gel makes the particles of silver chromate larger. The greater the number of carbon atoms in fatty acid is, the more remarkable this effect is. From Traube's rule, it is known that the higher the fatty acid is in the homologous series, the greater depression is caused in the surface tension of the solution. It may be supposed that from the jelly of lower surface tension the deposition of crystals is easier than from the jelly of higher surface tension. By the addition of a fatty acid, therefore, the supersaturation limit of crystallization of silver chromate falls steeply, and this makes the banding impossible. But, on the contrary, the solubility of the silver salt of the fatty acid decreases with the increase in the number of carbon atoms in the acid. So the banding of silver soap occurs and that of silver chromate appears as a secondary phenomenon.

The Effect of Alcohols. The experiments on the effects of the addition of alcohols to the gel have been undertaken with methyl, ethyl, propyl, and butyl alcohols. The number of bands was examined in about 4 per cent. gelatine jellies containing 0.25 mol. of alcohol per litre. The concentrations of upper and lower electrolytes were the same as in the experiments with

acids. It was observed that the number of bands did not change on addition of the alcohol to the gelatine jelly. However, when the concentration of the alcohol in jellies was 0.5 mol. per litre the effect of the alcohol became distinct. The results are shown in Table 1.

Table 1.

Dispersion medium	Number of bands formed	
	alcohol 0.25 mol./l.	alcohol 0.5 mol./l.
no alcohol	19	19
with methyl alcohol	19	25
with ethyl alcohol	18	25
with propyl alcohol	19	26
with butyl alcohol	19	—

Table 2.

Conc. of methyl alcohol mol./l.	Number of bands formed
0	28
0.25	28
0.50	30
1.00	31
2.00	33

The effect of the concentration of methyl alcohol in the jelly on the number of bands is shown in Table 2.

Thus, the higher the concentration of the alcohol is, the greater the number of bands formed. It was observed that the distance between the upper surface of the jelly and the last-formed band was shorter in the jelly with higher concentration of the alcohol.

In short, the addition of the alcohol to the jellies makes the crystallization of silver chromate easier than without the alcohol. This may be caused, on one hand, by the depression of the surface tension of the jelly, and, on the other hand, by the depression of upper limit of supersaturation of silver chromate crystals, owing to the less solubility of gelatine in the aqueous solution of the alcohol, that means the less protective action of gelatine than in water. The number of bands, therefore, must increase on addition of the alcohol.

The Effect of Amino-Acids. The surface tension of the aqueous solutions of some amino-acids were measured by Ito.[1] He showed that glycine and alanine, unlike other amino-acids, increased the surface tension of water. So the effect on banding of silver chromate may be in the opposite direction to the case of the alcohol, that is to say the distance between bands will be wider and the number of the formed bands will be smaller.

(1) Ito, *Nippon Nogei-kwagaku-kaishi*, **6** (1930), 178, 930.

This was verified by the experiments. One of the results obtained is tabulated in Table 3.

Table 3.

Dispersion medium	Number of bands formed
without amino-acid	28
with 0.05 mol. glycine per litre	24
with 0.05 mol. alanine per litre	26

Glycine increases the surface tension more than alanine does, so the effect of the former is more remarkable than that of the latter.

The Formation of Rhythmic Precipitates of Silver Soap. It has been described in the preceding paragraph that the bands of silver capronate or silver caprylate accompanies the silver chromate bands. Moreover, the author succeeded in obtaining the rythmic precipitates of silver soap only. Well dialyzed gelatine, freed from chlorides and phosphates, was dispersed into 4 per cent. sol, the acid was added, and then the whole was allowed to set. The concentration of the acid was between 0.05 and 0.1 mol. per litre. In the case of caprylic acid, an emulsion was formed. After setting the gel, 20 per cent. silver nitrate solution was poured on it. White thin bands appeared. The photograph shows an example of the bands of silver capronate. Thus two new examples of rhythmic precipitates were found, namely silver capronate and silver caprylate in gelatine jellies.

In conclusion the author expresses his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices.

Kochi High School,
Kochi.